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Phosphogypsum technology with the extraction of valuable components

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Abstract

Practically all phosphorites contain impurities whose presence is undesirable in fertilizers. At the same time it is necessary to extract rare earth elements from phosphorites. Every year millions of tons of phosphogypsum are sent to waste dumps that have an adverse impact on the environment. None of directions for reprocessing of phosphogypsum has been implemented in the industry yet. The paper presents the results of studies aimed at implementing the steps to obtain environmentally friendly waste from the production of fertilizers

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1. Introduction

Currently, Russia ranks second in the world reserves of rare earth materials, with a share of world reserves of 22%. In composition Russian raw material differs from that used in the world and it is a complete raw material from which rare earth elements are removed simultaneously, as one of components of the ore[1].

Table 1 presents the reserves of REE concentrates in the territory of Russia and the content of REE: Sm, Nd, Pr, Dy, Tb, required for the production of high-energy magnets[1, 2].

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Table 1. Estimated reserves and content of individual REM in concentrates

Raw material	Reserves of REO		Content of REO in ore, %	Content of individual oxide in Σ REO, %				
	mln. t	%		Sm	Nd	Pr	Dy	Tb
Loparite	6.4	30	32	0.9	14	6	0.12	0.3
Phosphorite	0.3	1.5	0.7	3.3	18.4	2.8	2.4	0.5
Apatite	10.8	50	1.0	2.1	13.9	4.9	1.1	1.0
Ittrosinhizit	0.3	1.5	45	3.2	9.7	3.3	4.4	0.7
Monazite	3.6	17	56	1.7	17.0	3.4	–	–
Orthite	0.05	–	30	0.4	3.2	1.0	0.5	0.1

Apatite refers to a mineral of a phosphate class: $3Ca_3(PO_4)_2 \cdot Ca(F,Cl,OH)_2$, impurities CO_3^{2-}, Mn, REE, U, Sr and others. The chemical composition of apatite and phosphorite ores, as the most promising source of REE is given in Table 2 [1–3].

Table 2. Averaged composition of apatite and phosphorite ores (*Note – REO – rare earth oxide*)

Component	REO*	CaO	Fe_2O_3	P_2O_5	SrO	SiO_2	F	TiO_2	ThO_2	Al_2O_3
Content, mass. %	0.1-l.0	50-52	3	30-40	2.8	1.9-2.7	2.8-3.5	0.3-0.6	$<10^{-3}$	0.45
Component	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Yb_2O_3	Y_2O_3
Content, mass. % in ΣREO	27.0	45.0	5.0	14.5	1.8	0.6	2.0	0.2	0.6	0.1	0.2	0.1	3.0

The data presented in Tables 1–2 shows that in Russia the greatest number of balance reserves of rare earth elements are concentrated in apatites. Apatites and phosphorites containing about 1.0% of REE could become one of the basic and readily available sources of REE, as their reprocessing volumes amount to 20 million tons/year, which corresponds to approximately 200 thousand tons/year of REE. They also have an advantage over loparite in composition and content of more valuable medium and medium-heavy REE. Besides, rare earth in them is in a readily retrievable form.

Practically all phosphorites contain impurities whose presence is undesirable in fertilizers. For example, Kingiseppsk phosphorite contains 2.6% (mass) of fluorine, Kovdorsk phosphorite contains 1.4, "Karatau" phosphorite - 2.3, Kola apatite - 3.2. At the same time it is desirable to extract from phosphorites such impurity as rare earth elements having a high cost. When obtaining fertilizers a part of impurities is converted to the calcium sulfate formed in large quantities during the opening of apatite with sulfuric acid. The bulk of the raw materials (85%) is reprocessed by sulfuric acid technology in options of the dihydrate or hemihydrate technology of the obtained phosphogypsum (PG). Form of resulting phosphogypsum depends on the process temperature and conditions of opening of apatite with sulfuric acid. To 90% of REE remain in gypsum when hemihydrate technology is used, when dihydrate technology is used, 20-30% of REE remain in wet-process phosphoric acid (WPA). Taking into account the scales of apatite reprocessing (8-10 mln./year), every year millions of tons of phosphogypsum are sent to waste dumps that have adverse impact on the environment. Despite the numerous studies carried out on this problem [1,2], the storage of phosphogypsum requires new plots of land.

All approaches to the phosphogypsum reprocessing can be reduced to the following options:

- use of phosphogypsum with small cleaning (rinsing with water, the addition of calcium oxide) in agriculture as a deoxidizer of soils, in building, in cement industry, etc.;
- intense impact on phosphogypsum with obtaining of high-quality gypsum for the manufacture of building mixes and products;
- targeted extraction of REE using leaching by mineral acid. Processing of phosphogypsum with sulfuric acid. In connection with the availability and cheapness of sulfuric acid a large number of studies are devoted to the use of sulfuric acid for converting of REE, contained in phosphogypsum, to aqueous solution.

- a resulting sulfuric extract is reprocessed by different methods and REE are extracted by sorption, precipitation, extraction;
- crystallization of double sulfates. One of the directions of the sulfuric option of phosphogypsum reprocessing consists in the extraction of REE in the form of double sulfates. A significant drawback of this technology is the use of highly concentrated sulfuric solutions. The question of the mother liquors utilization has remained unclear. Impurities will be accumulated in solutions that will necessarily require the purification of leaching solution. Besides, the variant of recrystallization of the hemihydrate to dihydrate is possible;
- deep reprocessing of phosphogypsum with obtaining of commercial products of varying degree of liquidity (ammonium sulphate, chalk, REE concentrates, potassium sulfate, etc.) - a significant number of technical solutions has been proposed in the direction of the full use of all the components present in the phosphogypsum. Within this direction a phosphogypsum is considered as a complex chemical feedstock containing such valuable components, as strontium, rare earth elements and calcium compounds. A common drawback of all the methods envisaging a complete decomposition of phosphogypsum is a significant energy cost (in calcination of carbonates) and low liquidity of such large-tonnage products, such as sodium sulfate and calcium carbonate. Furthermore, large number of operations of mainly periodic nature are typical for such technologies, which complicates the feasibility of these techniques in the industry;
- microbiological methods of REE extraction. A common drawback of these processes consists in the excessive length of the processes and the impossibility of complete cleaning from such environmentally harmful element in phosphogypsum as fluorine.

The most well-known reprocessing technology of phosphogypsum includes the operation of processing with sulfuric acid followed by various variants of REE extraction from the resulting solution, which comprises: REE 1-3 g/L of sulfuric acid, 0.5-1.0 mol/L, 5-10 g/L of phosphate-ion and 2.6 g/L of fluoride-ion. The main problem of this approach lies in the fact that the question of the utilization of administered sulfuric acid (at least 30-50 kg per 1 ton of phosphogypsum) has not been solved.

Let us note that none of the directions of phosphogypsum reprocessing has been realized in the industry yet. Perhaps this is due to the fact that these directions are either too narrowly solve an assigned task or solve it fully, but with heavy expenses and with obtaining of not very liquid products. It should also be noted that in most cases the phosphogypsum reprocessing issues are resolved in isolation from primary production up to the local organization of phosphogypsum reprocessing with no connection to the plants reprocessing apatite. At the same time, the plants reprocessing phosphorus-containing raw materials using sulfuric technology should be concerned about the wastes of their production to be environmentally friendly products. These issues are fundamental when considering the possibility of phosphogypsum reprocessing with extraction of a number of valuable components, rather than the issues related to the technology of REE extraction from phosphogypsum, recrystallization of phosphogypsum, etc.

Besides, the main problem is to obtain environmentally friendly waste from the production of fertilizers, and therefore the sequence of solutions of the problem must include the following steps:

- obtaining of environmentally friendly phosphogypsum - waste from the production of fertilizers;
- also, this technology should be an integral part of the overall technology of fertilizer production and, naturally, it should be located in the territory (or near) of the appropriate plant;
- the technology should not be unprofitable and, if possible, it must lead to the production of liquid products.

The stages are listed in descending order of their importance. At that an important role is given to the plants reprocessing apatite as the manufacturer of wastes – phosphogypsum. This article presents the results of studies aimed at the implementation of these stages.

2. Experimental part and discussion of the results

To carry out experiments we used phosphogypsum containing (% mass.): P_2O_5 – 0.8, fluorine – 0.4, CaO – 39.5, oxides REE – 0.6. To remove the impurities of fluorine and phosphorus, we chose the option of thermal influence with sulfuric acid, as the cheapest and most useful variant in the manufacture.

We have experimentally shown the expediency of processing of 2-3 phosphogypsum batches with the same sulfuric acid solution when heating to temperatures of 70-100 °C within 1-2 hours at S:L ratio of = 1:(1-3). The process was conducted under stirring and feeding (bubbling) of the air into the pulp. For opening a solution

containing 0.3-0.6 mol/L of sulfuric acid was used. After completion of the process a purified phosphogypsum was processed with a pulp of calcium oxide to a pH of 6.5-7.5. Filtrates and washing solutions were used to rinse the precipitation in the previous operations. Increase in the S:L ratio in favor of the aqueous phase, which is greater than 3.0, in processing of phosphogypsum with sulfuric acid is undesirable due to the difficulty of subsequent utilization of large volumes of aqueous solutions. Decrease in S:L ratio to 1 or less results in getting of a viscous pulp, particularly in the processing of dried phosphogypsum.

Thermal processing of phosphogypsum with sulfuric acid facilitates the recrystallization of phosphogypsum with obtaining of crystals of calcium sulfate, suitable for the production of building materials. The resulting phosphogypsum contains no harmful impurities and can be used in road construction, as additives in the production of cement and for the production of various building materials, etc.

We propose to carry out the processing of phosphogypsum with sulfuric acid in two variants: a part of phosphogypsum is processed in reactors at a temperature not exceeding 100 °C, a smaller part is autoclaved at a temperature of 130-150 °C with recrystallization of phosphogypsum. The conditions of processing in autoclaves should be selected separately for obtaining purified phosphogypsum of a required crystal structure. Taking into account a lower productivity when using autoclaves, the most of phosphogypsum will be reprocessed in reactors. In both cases after processing a phosphogypsum should be rinsed with water and the combined filtrate and rinsing waters should be sent for disposal of sulfuric acid.

In one of the experiments 100 ml of sulfuric acid at a concentration of 0.4 mol/L was added to 50 g of phosphogypsum. The pulp was heated for 2 hours at a temperature of 95-100 °C with stirring and air bubbling. After 2 hours the pulp was filtered and the precipitation was rinsed with 70 ml of water, which was sent to prepare a new portion of leaching solution. Rinsed precipitation was mixed with 0.1 g of calcium hydroxide to pH 7.4, and was removed as a finished product - purified phosphogypsum. Mass of purified (dried) phosphogypsum is 51.7 g, the content of impurities is shown in Table 3.

For disposal of sulfuric acid we have suggested to neutralize acid with apatite, i.e. to implement the process, which is reverse to the process of primary production - opening of apatite with sulfuric acid. When adding the apatite a secondary phosphogypsum is formed by the reaction:

$$5H_2SO_4 + Ca_5F(PO_4)_3 = 5CaSO_4 + 3H_3PO_4 + HF. \quad (1)$$

Mass of secondary phosphogypsum is 5-7% of the initial amount, and it depends on the amount of sulfuric acid in the leaching solution. Addition of apatite to a leaching solution allows to use sulfuric acid introduced into the process in the most economical way - for the reprocessing of raw materials - apatite with obtaining of an additional product (as well as, in the basic operation of the plant, processing apatite by sulfuric technology). There were fears that when adding apatite to the sulfuric solution of REE (from leaching of primary phosphogypsum) the sulfates of REE will be coprecipitated with calcium sulfate formed. As demonstrated by our experiments, when adding calcium oxide, about 5-10% of REE is coprecipitated, and when adding apatite to the similar solutions with a calcium sulfate formed, somewhat more REE is coprecipitated - up to 10-15%. Apatite was added to a sulfuric filtrate when S:L ratio was equal to 1:(10-20), neutralizing sulfuric acid to the content not less than 0.1 mol/L, at a temperature of 50-70 °C, and under stirring for 1-2 hours, the precipitation of secondary phosphogypsum was separated by filtration and sent to the head of the process.

Table 3. Content of impurities in purified phosphogypsum

Impurity	% mas.	Impurity	% mas.
P_2O_5	<0.1	U	<0.02
F	<0.1	Cd	<0.02
V	<0.02	Sb	<0.02
Cr	<0.02	Co	<0.02
MnO	<0.02	Ni	<0.02
Hg	<0.02	Zn	<0.02
As	<0.02	Pb	<0.02

Th	<0.02

From the filtrate obtained after the separation of secondary phosphogypsum, REE were precipitated with ammonia or ammonium hydroxide at pH = 3.0–3.5. Together with REE such elements as iron, aluminum, titanium, fluorine and phosphorus were precipitated. When reprocessing phosphogypsum obtained from phosphate not containing or containing a small amount of REE, precipitation was carried out to remove undesirable impurities (iron, aluminum, titanium, etc.) from the process. The value of pH of REE precipitation from leaching solution depends on the concentration of phosphate- and fluoride-ions in a solution (the content of these ions is determined by the amount of fluorine and phosphorus in the initial phosphogypsum and by the amount of apatite administered). The higher the concentration of phosphate-ions, than at lower pH values the hydrate phosphates of REE start precipitating and vice versa. The influence of pH on the REE precipitation rate from the leaching solution is given in Table 4.

Table 4. The influence of pH on the REE precipitation rate from the leaching solution of phosphogypsum, when a content of sulfuric acid in solution is 0.1 mol/L; REE – 1.7 g/L; R_2O_5 – 22 g/L

No. of experiment	pH	Content of REE in filtrate, g/L	Extraction of REE in precipitation, %
1	1.06	1.7	0
2	1.52	1.7	0
3	2.73	0.3	82.3
4	3.10	<0.1	>94
5	3.52	<0.1	>94

The content of REE oxides in the resulting precipitations amounts to 15–20% mass.

After separation of precipitation of REE, the filtrate containing ammonium phosphate was sent to the main production to rinse phosphogypsum after separating of extraction phosphoric acid (EPA). The peculiarity of the proposed technical solutions lies in the fact that the costs for heating of phosphogypsum pulp with sulfuric acid is compensated by subsequent using of mother liquors heated to accelerate the decomposition of apatite administered. Economic efficiency of the proposed method is provided by optimal use of resources – a sulfuric acid administered into the process for processing of phosphogypsum is fully used. Additionally 5-7% of apatite is reprocessed with obtaining of ammonium phosphate. A concentrate of valuable rare earth elements is extracted. The resulting purified phosphogypsum does not represent an environmental hazard and can be used in various industries.

3. Conclusions

In this paper we have proposed a method for reprocessing of phosphogypsum with the extraction of REE, which allows to obtain environmentally friendly phosphogypsum. The method includes an operation of sulfuric processing of phosphogypsum when heating to temperatures of 70-100 °C for 1-2 hours at a S:L ratio=1:(1-3) and bubbling of air into the pulp. The resulting phosphogypsum contains no harmful impurities and can be used in road construction, as additives in the production of cement and for the production of various building materials, etc. The peculiarity of the proposed technical solutions lies in the fact that the costs for heating of phosphogypsum pulp with sulfuric acid is compensated by subsequent using of mother liquors heated to accelerate the decomposition of apatite administered. Economic efficiency of the proposed method is provided by optimal use of all resources:

- sulfuric acid remaining after the opening of phosphogypsum is used for reprocessing of apatite;
- energy consumption for heating the pulp in the primary processing of phosphogypsum is reused for the decomposition of apatite;
- a liquid product is obtained in the process: eco-friendly (purified) phosphogypsum and concentrate of REE.

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References

1. I.F. Mulyarchuk. Chemical technology 1978; 2; 12-14.
2. A.L. Goldinov, S.D. Moiseev, F.I. Novoselov, et al. Isolation of phosphates of rare earth elements in the nitric acid processing of apatite. *Chemical Industry* 1980; 4; 33-34.
3. V.G. Kazak, N.S. Melnikov, V.D. Dmitriev, N.N. Konyuchenko. Trial verification technology to extract rare earths from apatite concentrate. *Chemical technology* 1983; 1; 13-15.
4. V.N. Lebedev, E.P. Lokshin. *The method of extraction of rare earths from phosphogypsum*. RF Patent No. 2158317. Patent class C22B59/00; 1999.
5. E.P. Lokshin, V.T. Kalinnikov, et al. *A method for the extraction of rare earths from phosphogypsum*. RF Patent No. 2293781. Patent class C22B59/00; 2005.